

such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 µg NO₂ standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K_c . Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO₃ working standard solution (1 ml = 100 µg NO₂) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in Section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in Section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400 µg NO₂) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in Section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds A_v , the absorbance of the 400-µg NO₂ standard (see Section 10.2.2).

11.4 Audit Sample Analysis.

11.4.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

11.4.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

11.4.3 The same analyst, analytical reagents, and analytical system must be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

11.5 Audit Sample Results.

11.5.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

11.5.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.5.3 The concentrations of the audit samples obtained by the analyst must agree within 5 percent of the actual concentration. If the 5 percent specification is not met, re-analyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.5.4 Failure to meet the 5-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may

also choose to use the data to determine the compliance or noncompliance status of the affected facility.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Nomenclature.

A = Absorbance of sample.

A₁ = Absorbance of the 100-μg NO₂ standard.

A₂ = Absorbance of the 200-μg NO₂ standard.

A₃ = Absorbance of the 300-μg NO₂ standard.

A₄ = Absorbance of the 400-μg NO₂ standard.

C = Concentration of NO_x as NO₂, dry basis, corrected to standard conditions, mg/dsm³ (lb/dscf).

C_d = Determined audit sample concentration, mg/dscm.

C_a = Actual audit sample concentration, mg/dscm.

F = Dilution factor (*i.e.*, 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of the calibration).

K_c = Spectrophotometer calibration factor.

m = Mass of NO_x as NO₂ in gas sample, μg.

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

RE = Relative error for QA audit samples, percent.

T_f = Final absolute temperature of flask, °K (°R).

T_i = Initial absolute temperature of flask, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_{sc} = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$\begin{aligned} V_{sc} &= (V_f - V_a) \frac{T_{std}}{P_{std}} \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \quad \text{Eq. 7-2} \\ &= K_1 (V_f - 25) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \end{aligned}$$